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Study Of Electron Impact Ionization Rate Coefficient

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Abstract:

In the interface of solid and liquid the discharge takes place when dc potential applied across solid and liquid interfaced electrodes. We study theoretically during discharge, ionization processes of atoms and ions, auto ionization, photoionization, transfer of energy which leads to Penning reaction, transfer of charge which leads to Duffendack reaction and also find out their ionization rate coefficients. The plasma parameters of electrons are significant factors for computing rate coefficients. We study theoretically electron impact ionization rate coefficients.

Keywords: Interface, ionization, discharge, rate coefficients, electron impact

Introduction:

The discharge column consists of electrons and the ions of metallic elements contained in the electrolytic solutions with different charges. The ions and electrons undergo collisions among themselves and with walls of the discharge column. The collisions between atoms and atoms, atoms and ions, ions and ions, atoms and electrons, ions and electrons are possible which result increase or decrease in their charge by unity. When the ion of charge Z is produced from the ion of charge Z-1 the process is called ionization whereas the ion of charge of Z is produced from the ion of charge Z+1 the process is called the recombination. Many times the collisions do not change the charge of the colliding particles but causes to change energy of the particles. These types of collisions cause excitations of the particles or the kinetic energy of the particles undergo some change. The probability of ionization and the probability of excitation depend upon the energy of incident electron. M.H.Elghazaly et al. (2007) have studied [1], the most important rate coefficients for electron collisions in noble gases, electron-neutral ionization and electron impact excitation [1]. They studied electron-neutral ionization besides electron impact excitation of some states of the argon and helium atom in DC glow discharge plasma. Electron properties as well as the calculated rate coefficients (ionization and excitation) were studied as a function of the axial distance from the cathode while the discharge operating parameters of voltage and pressure were varied [1]. S W Simpson et al. (1990) have studied ionization and recombination rates in argon plasmas [2]. They presented approximate model for treating multi-step ionization and recombination in inert gas plasmas [2].

Material and Methods:

In the solid and liquid interface discharge the metal ions of charge Z are produced by the ionization of the metal ions of charge Z-1. The metal ions of charge Z may also be produced by recombination of electrons with the metal ions of charge Z+1. Possible ionization processes are i) Ionization processes of atoms and ions ii) Autoionization iii) Photoionization. Cowan and Mann [3] considered the contribution of the autoionization process in the ionization of the atom or ion. They have calculated the autoionization rate for Na-like ions and found that the autoionization rate increases the ionization rate by a factor up to 2.5 and the effect of auto ionization may be treated separately. They concluded that the autoionization is an important process in Cu-like and Zn-like ions.

The Penning reaction

There is an important class of inelastic collisions between zinc atoms and atoms like helium atoms in excited states where potential energy of helium atom is transferred to zinc atom and zinc atom may get excited to upper state. The cross-section for this process is generally larger than that of other inelastic collisions between atoms or ions. Here excitation energy gets exchanged between neutral atoms. In particular, an excited atom can ionize by virtue of its excitation energy, if the later is larger than the required ionization energy. Such a process is made more probable if the excited helium atom is in a metastable state and has thus a longer lifetime within which it undergoes effective collision [4]. The process is then known as the Penning effect and can be an important ionizing agent for discharges in mixtures containing the rare gases, the atoms of which have metastable states of higher energy like helium. This process of transfer of energy is called as Penning transfer. Mathematically this process may be written as

$$\mathrm{HeI}^{*} + \mathrm{ZnI} \rightarrow \mathrm{HeI} + \mathrm{ZnII} + e^{-}$$

The ZnII ions produced during the process may be in the ground state or in excited state.

Duffendack Reaction (Charge transfer)

Charge transfer is the limiting case of Penning reaction [4]. An ion and a neutral atom collide and exchange the positive charge, the ion taking an electron from the atom. If the ion and the atom are of kind, so that no adjustment in total internal energy results, the particles continue to remain with the unchanged kinetic energy. This gives the appearance of a simple exchange of kinetic energy between atom and ion, so that fast ions appear to be slowed down, while slow atoms are speeded. Charge transfer is important when ions are moving through a gas under the influence of an electric field [4]. In the discharge like He-Zn the HeII ion transfers its energy to a zinc atom and result in zinc ion and helium atom. The zinc ions so produced are either in the ground state or in excited state. The process is called as Duffendack reaction or the charge transfer process as the charge on helium ion is simply transferred to zinc ion. The reaction may be expressed mathematically as

$$\text{HeII} + \text{ZnI} \rightarrow \text{ZnII}^{*} + \text{He}$$

The ions so produced decay spontaneously or by other process and come to ground state. These ions coming to ground state add to the ionization rate.

Electron Impact Ionization:

Electron impact ionization takes place as a result of collision between the high-energy electron and the zinc atom. An electron can excite or ionize an atom provided that its K.E. is sufficient to provide the necessary energy difference between electron levels. If E_{mn} is the energy required to raise a valence electron of an atom from level m to level n, and if E_1 is the kinetic energy of a colliding electron, then an inelastic collision can take place and the transition of atoms from m state to n state may take place if $E_1 > E_{mn}$. The cross-section of the atom for the transition by electron collision is zero for $E_1 < E_{mn}$, rises from this point to a maximum as E_1 increases, and falls again at higher electron energies [4].

Mathematical Formulation:

Ionization rate and Rate coefficients

Though the different ionization processes are possible, the probability of a particular process depends on its ionization cross-section. Therefore the following cross sections need to be considered.

By using the excitation cross-section and the corresponding energy values the excitation rate coefficients can be evaluated. These rate coefficients provide the idea of probability of a particular excitation reaction.

Penning Ionization Rate coefficients

The rate of production of Zn II by Penning process depends upon the neutral zinc density, the density of helium atoms in metastable states and the Penning rate coefficient P. The ionization rate by the process of Penning transfer may be expressed by

$$\frac{dN_{znII}}{dt} = N_{HeI} * N_{znI} P$$

Where P is the Penning reaction rate coefficient.

The Penning reaction rate coefficient P is dictated by the gas temperature and reaction cross-section. The gas temperature governs the number of effective collisions between zinc and helium metastable atoms.

The two elements in the mixture of helium and zinc are at the same temperature in the discharge column because the plasma is collisional. As the zinc (mass number is 65) is about 16 times heavier than helium (mass number is 4), the mobility or thermal velocity of it is negligibly smaller than the velocity of helium atoms. Hence in the calculation of the Penning rate coefficient the velocity of helium atoms, may be considered as effective velocity. The rate coefficient P, the reaction cross-section σ_p, and the thermal velocity v_{He} are related by

$$P = \frac{6.7x10^{7}}{86(\theta)^{3/2}} \int_{0}^{\infty} \sigma_P E \exp(-\frac{E}{\theta}) dE \ \mathrm{cm^3.sec^{-1}}$$

θ is the gas temperature in eV
σ_p is the Penning transfer cross-section in cm^2
E is the energy of helium atom in eV
and the factor 86 comes because of helium mass (4amu). However, it is more convenient to express the gas temperature in degree kelvin. Moreover, the Penning transfer cross-section does not depend upon the velocity of colliding helium atoms [5,6]. Hence Penning transfer rate coefficient reduces to,

$$P = 7.79 \times 10^5. \sigma_p (\theta)^{1/2} \mathrm{cm^3/sec} \qquad (A)$$

In the above equation the gas temperature is in eV. However, it is more convenient to express the gas temperature in degrees kelvin. This can be done by replacing θ by (θ/11600) in the equation (A) so that it reduces to

$$P = 7.23x\ 10^3 \sigma_p (\theta)^{1/2} \mathrm{cm^3/sec} \qquad (B)$$

Where θ is in degrees Kelvin.

L.D.Schearer and F.A.Padovani [5] have measured the total transfer cross-section σ_p for helium atoms and cadmium atoms by the pulsed afterglow technique. The value measured by them is 4.5x 10^{-15}cm^2. Experimental measurements of the Penning transfer cross-section for the He, Ne, Ar and Kr metastable states with Zn and Cd atoms have been carried out in a pulsed afterglow by L.A.Liseberg, W.F.Parks and L.D. Schearer [7] in 1973. They have provided, in tabular form, the experimental Penning cross-sections for noble gas metastable atoms with the Cd and Zn atoms. There is significant difference between the cross-sectoins of Penning transfer of zinc atom with various metastable atoms. Penning ionization cross-section for He-Zn is 2.91x10^{-15} cm^2 [7]. Substituting this value of σ_p, in equation (B) and can be written as

$$P = 2.10 \times 10^{-11} (\theta)^{1/2}$$

Inaba et al. [8] in the year 1981 have measured the Penning transfer cross-section of the individual level of cadmium ion. They have normalized the values to the value measured by Schearer and Padovani et al.[5]. Baltayan et al. [9] have measured the Penning excitation cross-sections of the individual level of cadmium ions and showed that the cross-section depends upon the angle at which the collisions takes place and the values differ slightly from the values obtained by Inaba et al.[8]. Both the groups have normalized the cross-section to the values measured by Shearer and Padovani [5]. The total rate of transfer of the energy from the helium metastable state to the cadmium ions is shared by the energy states of cadmium lying energetically below the energy of metastable state. Thus the excitation rate of the individual level is less than the total Penning transfer rate. Similarly in the He-Zn discharge the total number of zinc ions excited by Penning transfer would be distributed among the ZnII levels lying below the energy of the metastable state of helium. Therefore the rate of excitation of the individual energy states by the Penning transfer is less compared to the total excitation rate.

Duffendack reaction Rate Coefficient

The process of ionization due to charge transfer or Duffendack reaction has been already explained. The rate of production of ZnII ions by the Duffendack reaction depends upon the zinc atom density, helium ion density and the rate coefficient T of Duffendack process. The rate of ionization by the Duffendack process is expressed as :

$$\frac{dN_{znII}}{dt} = N_{znI} * N_{HeII} T$$

The rate coefficient of the Duffendack process is average value expressed as:

$$T = < V_{He} \sigma_T >$$

σ_T is the cross-section of the charge transfer and V_{He} is the velocity of helium atoms relative to the zinc atoms.

The ionization rate coefficient can be expressed in terms of energy of helium atoms, the gas temperature θ and the cross-section σ_T as

$$T = \frac{6.7 \times 10^7}{86\left(\theta^{3/2}\right)} \int_0^\infty \sigma_T E \exp(-E/\theta) dE \quad cm^3.sec^{-1}$$

At present the data of cross-section related to velocity dependence [5,6] of the charge transfer cross-section is not available. Therefore σ_T can be taken out of integration and we can write the equation as

$$T = \frac{7.79 \times 10^5}{\theta^{3/2}} \sigma_T \int_0^\infty E \exp(-E/\theta) dE \quad cm^3.sec^{-1}$$

By putting the value of the standard finite integral, it reduces to

$$T = 7.79 \times 10^5 \sigma_T (\theta)^{1/2} \qquad \text{(C)}$$

This equation is the same as equation for Penning ionization rate coefficient except the term σ_T in place of σ_P. A.R.Turner-Smith, J.M.Green and C.E.Webb [10] have measured the relative cross-section for excitation of various final states of the metal atom/ rare gas ion reaction using after glow technique of Fergusson et al.[11]. They [10] have studied the thermal energy charge transfer reactions of He^+ with Zn, Cd and Se, and Ne^+ with Mg. The largest reaction rates are found to be those for the levels of the product ion lying some 0.1-0.4 eV below exact resonance. From the experimental [10] result the maximum value of cross section for the charge transfer reaction is 1.53×10^{-14} cm^2. Substituting this value for σ_T in equation (C) and converting θ from eV to degrees kelvin by using the proper convertion factor, the equation (C) reduces to

$$T = 1.11 \times 10^{-10} (\theta)^{1/2}$$

The ionization rate of ZnI by Penning transfer and Duffendack reaction may be compared by computing the cross-sections for the corresponding processes as the equations are similar to each other.

Result & Discussion:

Electron impact ionization rate coefficients

The plasma parameters of electron are significant factors for computing the rate coefficients [3]. The process of electron impact ionization is the ultimate result of collision between a high-energy electron and neutral atom says zinc. As the velocity of electron is much greater than the zinc atom, the electron impact ionization rate coefficient S_z is function of the i) electron velocity distribution, ii) electron energy and iii) electron impact ionization cross-section σ_z. It can therefore be expressed by an equation

$$S_z = < \sigma_z v_e >$$

It is clear from the equation that S_z can be determined if the velocity distribution of electrons and the ionization cross-section as a functions of electron energy are known.

While studying the spectral emission of corona, Seaton [12,13] has developed a theory and proposed an expression for obtaining ionization rate coefficient which depends upon ionization potential I and the electron temperature T and is written in the form

$$Sz = 2.0 \times 10^{-8} (\zeta / I^2) T^{1/2} 10^{-5040(I/T)} \text{ cm}^3 \text{ sec}^{-1}$$

ζ is the number of equivalent electrons in the outermost shell from where ionization takes place,

I is ionization potential in eV,

T is electron temperature in degrees kelvin.

It is believed that this formula gives spurious results and hence may not be considered for the calculations of ionization rate coefficients. The empirical formula for the electron impact ionization rate coefficient has been proposed by Wilson and White [14] which is expressed below,

$$S_Z = \zeta \frac{0.90 \times 10^{-5}}{\chi^{3/2}} \times \frac{\sqrt{(kT_e / \chi)}}{(4.88 + kTe/\chi)} \exp(-\chi / kT_e) \; cm^3 \; sec^{-1}$$

χ is the ionization potential in eV

T_e is electron temperature in degree kelvin,

ζ is the number of electrons in outermost orbit.

The semi-empirical formula for electron impact ionization cross-section has been proposed by Lotz [15-17] and is expressed as

$$\sigma = \sum a_i \chi_i \ln \frac{\left(\frac{E}{p_i}\right)}{Ep_i} \left[1 - b_i \exp(-c_i \left(\frac{E_i}{p_i} - 1 \right)) \right] \quad \text{cm}^2$$

E is the energy of the electron,

p_i is the binding energy of the electron which is to be removed,
χ_i is the number of equivalent electrons in the ith subshell,
a_i, b_i, c_i are constants to be determined either by experimental work, theory or by guess-work.

The derivation of the rate coefficients from the cross-section depends upon the electron velocity distribution. Gill and Webb [18] have extensively studied the electron energy distribution and showed that the electron energy distribution does not follow the Maxwellian distribution. The electron velocity distribution show high energy tail, but in positive column discharge the electron energy distribution is very near to Maxwellian. They have [19] further obtained the relation for zinc ion density assuming the Maxwellian distribution for electron energy. The density of electrons having an energy between E and E+dE which follow the Maxwellian distribution function and it is given by

$$\frac{dn}{n}=\left(\frac{2}{KT_e}\right).\left(\frac{E}{\pi KT_e}\right)^{1/2}\exp\left(-\frac{E}{KT_e}\right)dE$$

n is the number of electrons having energy between E and E+dE,
T_e is the electron temperature in degree Kelvin.

For the Maxwellian velocity distribution, the electron impact ionization rate coefficient by electron collision using Lotz cross section for ionization is

$$S_Z = 6.7x10^7\sum_{i=1}^{N}\frac{a_i\xi_i}{T_e^{\;3/2}}\{\frac{1}{P_i/T_e}\int_{P_i/T_e}^{\infty}\frac{e^{-x}}{x}dx$$

$$-\frac{b_i\exp(c_i)}{P_i/T_e+c_i}\int_{P_i/T_e+c_i}^{\infty}\frac{e^{-y}}{Y}dy\}\ \mathit{cm^3\,sec^{-1}}$$

T_e - electron temperature in eV.

P_i - number of equivalent electrons in the subshell.

ζ_i is the number of equivalent electrons in this subshell.

The lower limit of integration depends upon the electron temperature and ionization potential. The contribution of the second term may be neglected, when compared to the first term, due to very small values of the constants b_i and c_i. The final expression for electron impact ionization rate coefficient may be written as

$$S_Z = 6.7x10^7\sum_{i=1}^{N}\left(\frac{a_i\xi_i}{T_e^{\;3/2}}\right).\left(\frac{1}{\left(\frac{P_i}{T_e}\right)}\right).\int_{P_i/T_e}^{\infty}\frac{e^{-x}}{x}dx \quad \mathrm{cm^3\,sec^{-1}} \qquad \text{(D)}$$

The effect of the removal of the electron from the inner orbits on the ionization rate coefficient has been considered by Lotz [15-17]. The value of the integral for the inner orbit electrons is small. The rate of ionization by the removal of inner orbit electron is also small as usually expected.

Recently, it has been reported by Bolorizadeh et al. [20] that Lotz formula in equation (D) gives the values which are very close to the experimental values of the ionization cross section and therefore, can be used for the evaluation of ionization cross-section and hence rate coefficients [20]. However, Wilson and White formula also gives reasonably good results. Further, the Wilson White formula provides the result in short interval of time and therefore, it is used when a quick evaluation is required. As Lotz formula gives more correct results, it is more preferred in spite of the fact that it takes relatively longer time. Moreover, the Lotz formula for obtaining the cross-sections, works with all types of velocity distributions of the discharge electrons.

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